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Theoretical and experimental studies of the opto-electronic properties of positively charged oligo(phenylene vinylene)s: Effects of chain length and alkoxy substitution

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In this paper a combined experimental and quantum chemical study of the geometry and opto-electronic properties of unsubstituted and dialkoxy-sustituted phenylene–vinylene oligomers (PV's) is presented. The optical absorption spectra for PV cations with different chain lengths and substitution patterns were measured using pulse radiolysis with time-resolved spectrophotometric detection from 1380 to 500 nm (0.9 to 2.5 eV). The geometries of the PV's studied were optimized using density functional theory (DFT) for both the neutral and singly charged molecule. The spectra for the PV radical cations were then calculated using singly excited configuration interaction with an intermediate neglect of differential overlap reference wave function method together with the DFT geometry. The agreement between experimental and theoretical absorption energies is excellent; most of the calculated radical cation absorption energies are within 0.15 eV of the experimental values. The pattern of dialkoxy-substitution is found to have a large effect on the optical absorption spectrum of the cation. Using the calculated charge distribution it is shown that the degree of delocalization of the charge correlates with the energy of the lowest absorption band. If alkoxy side chains are present on some of the rings the positive charge tends to localize at those sites. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1522374]

I. INTRODUCTION

Conjugated polymers have an alternating sequence of single and double bonds, giving rise to π-orbitals that are delocalized over several monomer units. In general these materials are wide band-gap semiconductors in their pristine state, but can become conducting on oxidative or reductive doping. Some members of this class of polymers emit light when electrons and positive charges are injected through electrodes. These physical properties, combined with the low cost and ready processability, make these materials interesting candidates for (opto)electronic applications such as field-effect transistors, light emitting diodes and photovoltaic cells.[1–3]

Poly(para-phenylene vinylene) (PPV) and its derivatives are conjugated polymers that have been studied extensively for an application as the emitting layer in light emitting diodes and solid-state lasers.[4,5] They are also being considered as the absorbing antenna layer in photovoltaic devices.[2,6] The first demonstration of a conjugated polymer light-emitting diode (LED) was based on an unsubstituted PPV[7] which is insoluble and thus excludes processability from common organic solvents. The attachment of substituents such as alkyl- and alkoxy side-chains provides soluble polymers that can be processed for instance by spin coating. The introduction of alkoxy groups also offers the possibility to tune the absorption and emission wavelength and improve the electroluminescence yield of LED's.[8–10]

The application of PPV's in LED's and photovoltaic cells relies critically on the ability of the polymer to transport charges. A detailed knowledge of the nature of charge carriers in PPV's is therefore essential. The properties of charged defects on phenylene vinylene chains have been studied experimentally by optical absorption measurements, ESR and vibrational spectroscopy.[11] Studies of well-defined phenylene–vinylene (PV) oligomers in solution have shown that the optical absorption spectrum of singly charged PV's is characterized by two electronic transitions below the lowest energy absorption band of the neutral compound. The assignment of these absorptions to the radical ions is sup-

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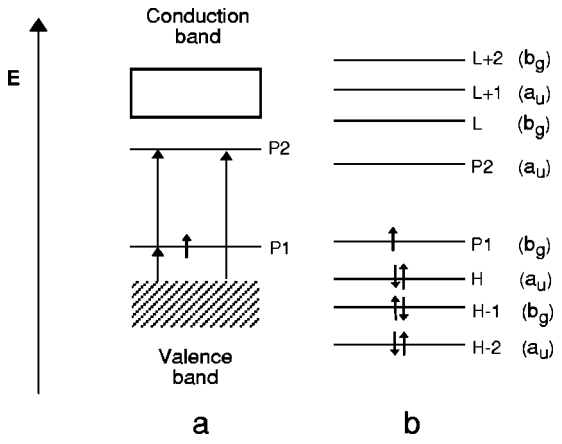

FIG. 1. Band structure model (a) and molecular orbital model (b) for sub-gap absorption features in singly charged phenylene vinylenes.

ported by an ESR signal that indicates the presence of an unpaired spin.[12] For doubly charged PV's the optical absorption spectrum has been predicted to exhibit a single strong transition.[13] Such an absorption feature has been observed for an oligomer containing three phenylene rings (PV2) in a doped solid film.[14]

The radical cation optical absorption spectra of conjugated polymers (and also of oligomers) are usually discussed in terms of a one-electron band structure model.[15] In this model the introduction of a localized, singly charged defect leads to the formation of two electronic levels inside the gap between the valence band and the conduction band [Fig. 1(a)] which are responsible for the sub-gap absorption features in the spectrum of the cation. The three possible sub-gap excitations are indicated by arrows in Fig. 1(a). A band structure model infers an infinitely long conjugated polymer chain with a periodic structure. However, the present work involves oligomers where discrete energy levels are present instead of bands, as indicated in Fig. 1(b). Moreover, even for polymers a band structure model is not directly applicable since polymers are usually rather disordered and consist of a distribution of conjugation lengths. Consequently, they usually have electronic properties that are more similar to that of a distribution of oligomers of different length, rather than those expected for an infinitely long periodic chain.[16] Although the band structure model is not directly applicable for oligomers the terminology is generally used and is therefore also adopted in this paper. In this terminology the lower ''polaron'' level, which is singly occupied, is called P1 and the lowest unoccupied level is called P2. Note that in this system the electronic level called LUMO or L is actually the second empty level while the HOMO level or H is the highest doubly occupied orbital, see Fig. 1(b).

Quantum chemical calculations can yield valuable information on the molecular level which cannot be obtained by experimental methods. Semi-empirical calculations on the formation of polarons on phenylene vinylene oligomers have been performed by Cornil *et al.*[13] From geometry optimizations using the AM1 method it was concluded that a positive charge on a PV chain is self-localized and its spatial extent was estimated to be *circa* three repeat units. The geometries obtained from these calculations were used to calculate the electronic spectra using the intermediate neglect of differential overlap Hamiltonian (INDO) combined with the singly excited configuration interaction (CIS) method, in the following the acronym INDO/s-CIS is used for this way of calculating the electronic spectra. The calculations indeed showed two allowed electronic transitions below the onset of the optical absorption of the neutral compound, however, the absolute agreement with the experimental absorption energies was rather poor. The work by Cornil *et al.* was also limited to unsubstituted PV's which makes a comparison to experimental work difficult since PV's and PPV's used in experimental work usually contain substituents, either to make them soluble or to tune their optical properties as mentioned above. The presence of side-chains can be expected to have a considerable effect on the spatial extent and optical absorption spectra of charges on PV chains.

Our aim in this paper is to provide insight into the effect of chain length and alkoxy substituents on the opto-electronic properties of singly positively charged PV oligomers. A combined experimental and theoretical study of the electronic structure and spatial extent of polarons on phenylene–vinylene oligomers is presented. Optical absorption spectra of positively charged oligomers have been measured by performing pulse radiolysis experiments for a variety of PV's differing in chain length and substitution pattern. The charge distribution and excitation energies of singly charged PV's are determined theoretically using a combination of density functional theory (DFT) and semiempirical INDO/s calculations. The geometry of neutral and charged PV's were optimized using DFT. These geometries were used in INDO/s-CIS calculations in order to calculate the optical absorption spectra of the cations. Excitation energies calculated for different chain lengths and a variety of substitution patterns are compared to optical spectra of radical cations obtained from pulse radiolysis experiments described here and to spectra previously reported in the literature. The results provide a unique insight into the subtle effects of substituents on the geometry and electronic structure of singly oxidized PV's. The structures of the phenylene vinylene derivatives investigated in the present work and their pseudonyms are shown in Fig. 2.

II. EXPERIMENTAL SECTION

The compounds PVn($n/2\,da$) and PV4($1\,da$) shown in Fig. 2 were synthesized and purified as reported earlier.[17,18] Solutions (*ca.* 10^{-4} M) in UV-spectroscopic grade benzene were freshly prepared before each experiment and bubbled with benzene-saturated oxygen for at least ten minutes. All experiments were performed at room temperature.

The pulse radiolysis method using transient optical absorption detection was essentially the same as used previously for the measurement of triplet spectra of the PVn($n/2\,da$) oligomers.[19,20] Solutions were irradiated using 50 ns pulses of 3 MeV electrons from a Van de Graaff accelerator in order to create PV radical cations as described in Sec. IV. The solutions were flowed continuously through a quartz cell (optical path length 12.5 mm) using a slight overpressure of benzene-saturated oxygen. The source of detec-

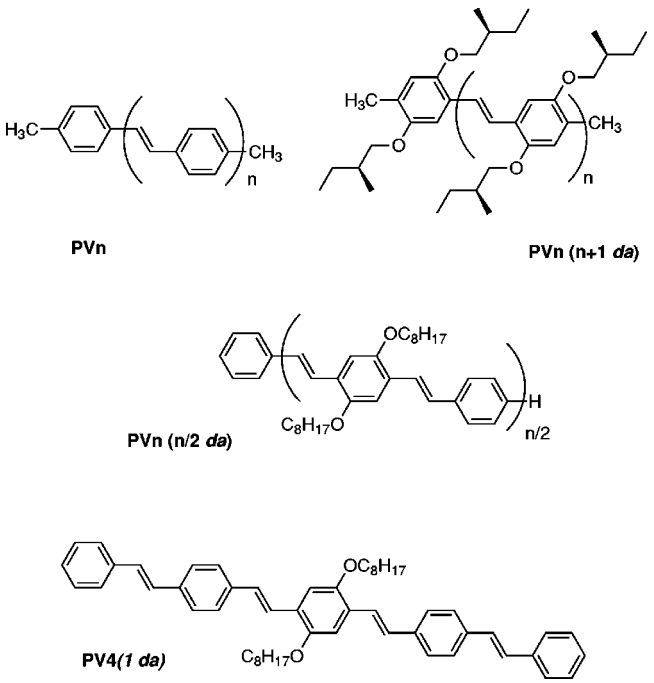

FIG. 2. Structures of the PV oligomers for which calculations have been performed. In this paper the notation PVn(x da) is used, in which n is the number of phenylene vinylene units (one less than the number of phenylene moieties) and x is the number of dialkoxy substituted phenyl rings.

tion light was a pulsed high-pressure Xe-lamp (450 W). Cut-off filters and a fast shutter were used to minimize photolysis of the solution by the detection light. NIR detection was achieved using a short-wavelength enhanced InGaAs photodiode (Hamamatsu, Japan). Transient changes in the optical absorption were recorded using a Tektronix TDS680 digitizer. The lower limit of the photon energy was *ca.* 0.9 eV.

III. COMPUTATIONAL METHODOLOGY

The geometries of all the phenylene–vinylene oligomers studied in this work were optimized using the Amsterdam density functional program (ADF).[21,22] The geometry optimizations were performed using the local density approximation (LDA) with the exchange and correlation functionals based on the parametrization of the electron gas data given by Vosko, Wilk, and Nusair (VWN).[23] Generalized gradient approximation corrections by Becke (exchange) and Perdew (correlation) were included.[24,25] All calculations were performed using a basis set of double-zeta quality including polarization functions (DZP, basis set III in ADF) consisting of Slater-type functions. Test calculations for short oligomers showed that there are no significant changes in geometry if a larger basis set is used. For the charged oligomers the restricted open shell method was used in order to avoid artifacts due to spin contamination. The geometries were restricted to C_{2h} symmetry.

The excitation spectra for the singly charged oligomers were calculated as follows. A restricted open shell Hartree–Fock (ROHF) calculation, using the intermediate neglect of differential overlap (INDO/s)[26–29] Hamiltonian, was performed for the ground state. The Coulomb repulsion terms were described using the Mataga–Nishimoto parameters which have been especially developed for spectroscopic calculations. The electronic spectra were obtained from singly excited configuration interaction (CIS) calculations using the ground-state ROHF wave function as the reference determinant. The smallest CI expansion used in the calculations contained all configurations involving single excitations from the 20 highest occupied molecular orbitals into the 20 lowest unoccupied molecular orbitals of the ROHF reference wave function. This was found to be sufficient for convergence of the excitation energies for oligomers with a chain length of up to 4 PV units. For longer oligomers it was found that larger CI expansions were necessary. The largest CI space used in this work contained all configurations involving single excitations from the 40 highest occupied molecular orbitals into the 40 lowest unoccupied orbitals, giving a total of 3200 configurations for the doublet multiplicity. The energy of the lowest allowed transition of the radical cation (RC1) was found to be less sensitive to the size of the CI expansion than those of transitions to higher states (RC2 and RC3). In the oligomers for which two or more close lying allowed transitions were calculated the convergence of the high energy transitions with the size of CI space was rather slow, especially with regard to the oscillator strength. The method for the calculation of spectra outlined here is known to give an excellent description of electronic spectra of neutral molecules if an accurate geometry is used.[28]

IV. RESULTS AND DISCUSSION

The phenylene–vinylene oligomers studied in this work are shown in Fig. 2. The oligomers include three series of increasing length. The first series consists of phenylene vinylene oligomers, PVn, which are para-substituted with methyl groups on the outermost phenylene rings. Experimental data on the optical absorption spectra of the cations of these oligomers up to $n=3$ is available from experiments by Furukawa *et al.*[14] (see Table I). The second series of oligomers, PVn($n+1$ da) contains two alkoxy substituents on all phenyl rings. Cation spectra for these oligomers are available from the work of Van Hal *et al.*[30] (see Table II) who studied photo-induced charge transfer between PV's and a fullerene derivative.

In the third series, PVn($n/2$ da), every other phenylene ring is substituted with two alkoxy side chains. The optical absorption spectra of the PVn($n/2$ da) cations were obtained from pulse radiolysis experiments performed in the present work (see Table III). In order to study the effect of substituents in more detail, experiments and calculations were performed on one more oligomer, PV4(1 da), which is dialkoxy substituted only on the central phenylene moiety.

A. Measurements of PV radical cation spectra

Irradiation of benzene (Bz) leads to the formation of radical cations (Bz^+), excited states (Bz*), and excess electrons (e^-),[31–33]

$$Bz \rightarrow Bz^+, Bz^*, e^-. \tag{1}$$

In oxygen-saturated solution ($[O_2]=11.9$ mM at 1 atm and 25 °C), the excited states and the excess electrons are scavenged within a few nanoseconds, Eqs. (2) and (3):

TABLE I. Calculated and experimental transition energies (ΔE_+), calculated oscillator strengths (f) and main CI expansion coefficients for radical cations of PVn oligomers. Only transitions with an oscillator strength higher than 0.1 are given.

Compound	Band	ΔE_+ (Exp.)[a] in eV	ΔE_+ (Calc.) in eV	f (Calc.)	Main CI-expansion coefficients
PV1	RC1	1.54	1.71	0.04[b]	-0.51(H-2→P1) -0.50(H→P1) $+0.52$(H→P2)
	RC2	2.45	2.20	0.80	-0.46(H-2→P1) -0.37(H→P1) -0.70(P1→P2)
PV2	RC1	1.03	1.13	0.36	-0.87(H→P1) -0.33(H→P2)
	RC2	1.95	1.89	1.01	-0.35(H→P1) $+0.78$(P1→P2)
PV3	RC1	0.80	0.87	0.62	-0.87(H→P1)
	RC2	1.74	1.69	1.14	0.77(P1→P2)
PV4	RC1	-	0.71	0.89	-0.87(H→P1)
	RC2	-	1.65	1.03	0.39(H→L) $+0.65$(P1→P2)
	RC3	-	1.91	0.22	0.52(H-2→P1) -0.49(P1→P2)
PV6	RC1	-	0.55	1.13	0.49(H-2→P1) -0.78(H→P1)
	RC2	-	1.44	0.14	0.35(H-6→P1) -0.48(H-2→P1)
	RC3	-	1.58	1.00	0.41(H→P1) $+0.63$(P1→P2)
PV8	RC1	-	0.49	1.29	0.33(H-4→P1) $+0.60$(H-2→P1) $+0.64$(H→P1)
	RC2	-	1.57	0.80	0.45(P1→P2)
	RC3	-	1.81	0.38	0.55(P1→P2)
PV10	RC1	-	0.46	1.33	
	RC2	-	1.47	0.23	
	RC3	-	1.60	0.27	
PV12	RC1	-	0.45	1.39	
	RC2	-	1.60	0.43	
	RC3	-	1.72	0.34	

[a]Experimental data were taken from Ref. 13.
[b]For unsubstituted PV2 the calculated oscillator strength was found to be smaller than 0.1.

$$Bz^* + O_2 \rightarrow O_2(^1\Delta) + Bz, \quad (2)$$

$$e^- + O_2 \rightarrow O_2^- . \quad (3)$$

The Bz^+ ions are unreactive towards O_2 and can diffuse to the dissolved PV oligomers where they undergo charge transfer [Eq. (4)], since these conjugated oligomers have a lower ionization potential than benzene. This results in the abstraction of an electron from the oligomer, forming the radical cation or ''hole:''

$$Bz^+ + PV \rightarrow Bz + PV^+ . \quad (4)$$

The absorption spectra of the radical cations were obtained by measuring the transient changes in the absorbance of the solution at different wavelengths. The absorption spectra obtained for the PVn($n/2\,da$) series are shown in Fig. 3. The energies at which the absorption maxima occur are listed in Table III.

For the radical cation of PV2($1\,da$) two well-separated bands are observed: one at 1.24 eV and the other at 2.03 eV. These bands are denoted RC1 and RC2, respectively. The appearance of two absorption maxima in the radical cation spectra of PV's is in agreement with earlier experiments[14] and quantum chemical calculations by Cornil *et al.*[13] For the longer oligomers in the PVn($n/2\,da$) series the low energy band, RC1, shifts below 0.9 eV and cannot be observed with the optical absorption setup used in the present work. The high energy absorption band, RC2, also shifts to lower energy when the chain length is increased but remains within

TABLE II. Calculated and experimental transition energies (ΔE_+), calculated oscillator strengths (f) and main CI expansion coefficients for radical cations of PVn($n+1\,da$) oligomers. Only transitions with an oscillator strength higher than 0.1 are given.

Compound	Band	ΔE_+ (Exp.)[a] in eV	ΔE_+ (Calc.) in eV	f (Calc.)	Main CI-expansion coefficients
PV2($3\,da$)	RC1	0.76	0.90	0.30	-0.85(H→P1)
	RC2	1.71	1.66	0.64	0.74(P1→P2) $+0.34$(H→P1)
	RC3	~2.0	1.99	0.23	0.78(H-2→P1)
PV3($4\,da$)	RC1	0.66	0.71	0.43	0.77(H→P1) $+0.42$(H-2→P1)
	RC2	1.52	1.34	0.34	0.37(H-4→P1) -0.41(H-2→P1) -0.51(P1→P2)
	RC3	~1.7	1.56	0.61	0.39(H→P1) -0.57(P1→P2) $+0.34$(H-4→P1) $-$ 0.44(H-2→P1)
PV4($5\,da$)	RC1	0.59	0.68	0.58	-0.77(H→P1) -0.40(H-3→P1)
	RC2	1.43	1.35	0.96	0.68(P1→P2)
	RC3	~1.6	1.61	0.11	-0.42(H-3→P1) -0.40(P1→P2)
PV5($6\,da$)	RC1	0.54	0.57	0.74	-0.73(H→P1) $+0.32$(H-4→P1) $+0.42$(H-2→P1)
	RC2	1.40	1.24	0.31	0.47(H-4→P1) -0.37(P1→P2)
	RC3	~1.6	1.40	0.85	0.39(H-4→P1)0.37(H→P1)0.65(P1→P2)

[a]Experimental data taken from Ref. 30.

TABLE III. Calculated and experimental transition energies (ΔE_+), calculated oscillator strengths (f) and main CI expansion coefficients for radical cations of PVn($n/2\,da$) oligomers. Only transitions with an oscillator strength higher than 0.1 are given.

Compound	Band	ΔE_+ (Exp.)[a] in eV	ΔE_+ (Calc.) in eV	f (Calc.)	Main CI-expansion coefficients
PV2(1 *da*)	RC1	1.26	1.26	0.04[c]	0.63(H→P1)+0.52(P1→P2)
	RC	2.07	2.02	1.08	0.63(H→P1)−0.61(P1→P2)
PV4(2 *da*)	RC1	-	0.51	0.75	−0.91(HP1)
	RC2	1.51	1.49	0.56	−0.33(H-2→P1)+0.62(P1→P2)−0.32(H→L)
	RC3	1.70	1.74	0.53	0.62(H-2→P1)+0.47(P1→P2)
PV6(3 *da*)	RC1	-	0.75	0.86	−0.77(H→P1)+0.33(H-4→P1)
	RC2	1.49	1.47	0.44	0.32(H-4→P1)
	RC3	1.61	1.56	0.72	0.44(H→P1)+0.63(P1→P2)
	RC4	-	1.91	0.30	0.42(H-4→P1)−0.34(P1→P2)
PV8(4 *da*)	RC1	-	0.38	1.03	−0.72(H-2→P1)+0.54(H→P1)
	RC2	1.51[b]	1.41	0.77	−0.52(P1→P2)
	RC3	1.51[b]	1.56	0.10	0.40(P1→P2)
	RC4		1.72	0.29	−0.41(P1→P2)+0.33(H-2→P1)−0.39(H−6→P1) +0.43(H-10→P1)
PV10(5 *da*)	RC1	-	0.66	1.08	
	RC2	-	1.47	0.30	
	RC3	-	1.65	0.81	
	RC4	-	1.92	0.49	
PV12(6 *da*)	RC1		0.34	1.15	
	RC2	1.49[b]	1.51	0.56	
	RC3	1.49[b]	1.59	1.19	
	RC4		1.72	0.38	
PV16(8 *da*)	RC2	1.48[b]	-	-	
	RC3	1.48[b]	-	-	
PV4(1 *da*)	RC1	~0.9	1.03	0.44	
	RC2	1.6	1.77	1.47	
	RC3	1.97	1.94	0.14	

[a]Experimental data obtained from spectra in Figs. 3 and 4.
[b]Could not be separated.
[c]For PV2(1 *da*) the calculated oscillator strength was found to be smaller than 0.1.

the detection range. Interestingly, this high energy band clearly exhibits two maxima for PV4(2 *da*) and PV6(3 *da*). These maxima are denoted RC2 and RC3 in Table III. The assignment of these bands to two separate electronic transitions is supported by the results from the calculations described in Sec. IV B. The energy difference between RC2 and RC3 decreases from 0.19 eV for PV4(3 *da*) to 0.12 eV for PV6(2 *da*). In the spectra for PV8(4 *da*) through PV16(8 *da*) only a single broad maximum can be discerned. In view of the results for the shorter oligomers this absorption band is considered to be due to the fusion of two individual electronic transitions at close lying energies. This combined absorption band RC2/RC3 exhibits only a very small spectral shift in going from PV4(2 *da*) to longer chains.

Figure 4 shows a comparison of the absorption spectra for the radical cations of PV4(2 *da*) and PV4(1 *da*). It is evident from this comparison that the cation optical absorption spectrum of a phenylene vinylene tetramer depends strongly on the number of alkoxy substituents and their positions. The low energy absorption band, RC1, which is below 0.9 eV for PV4(2 *da*) and could therefore not be observed in the present experiments, has moved to considerably higher energy in PV4(1 *da*). The RC1 energy is in fact close to that observed for PV2(1 *da*) which indicates that the charge carrier is more localized in these two compounds than in PV4(2 *da*). The RC1 band appears to be more sensitive to the delocalization length of the charge carrier than the RC2 or RC3 bands. The spectrum of PV4(1 *da*) exhibits a shoulder on the high energy side of RC2 which is attributed to the second high energy transition, RC3, as observed for the PV4(2 *da*) and PV6(3 *da*).

B. Calculated absorption spectra of PV cations

The electronic transitions of the radical cations of all PV oligomers shown in Fig. 2 have been calculated using the methodology outlined in Sec. III. For the calculations on these compounds, the alkoxy substituents were taken to be methoxy groups. This simplification is not expected to significantly influence the results with regard to electronic effects of the substituents. Of course bulky alkyl groups could possibly have a steric effect especially in the case of the PVn($n+1\,da$) series in the experiments of Van Hal *et al.*[30] since these contain branched alkoxy side chains on all phenyl rings. The PV1, PV2 and PV3 oligomers used in the experimental work of Furukawa *et al.*[14] contained two methyl groups, para-substituted on the outermost phenyl rings. These methyl groups were omitted in the calculations

The calculated radical cation transition energies are collected in Tables I–III together with the experimental data from the present pulse radiolysis experiments and values from the literature. The agreement between the calculated excitation energies and the experimental data is in general

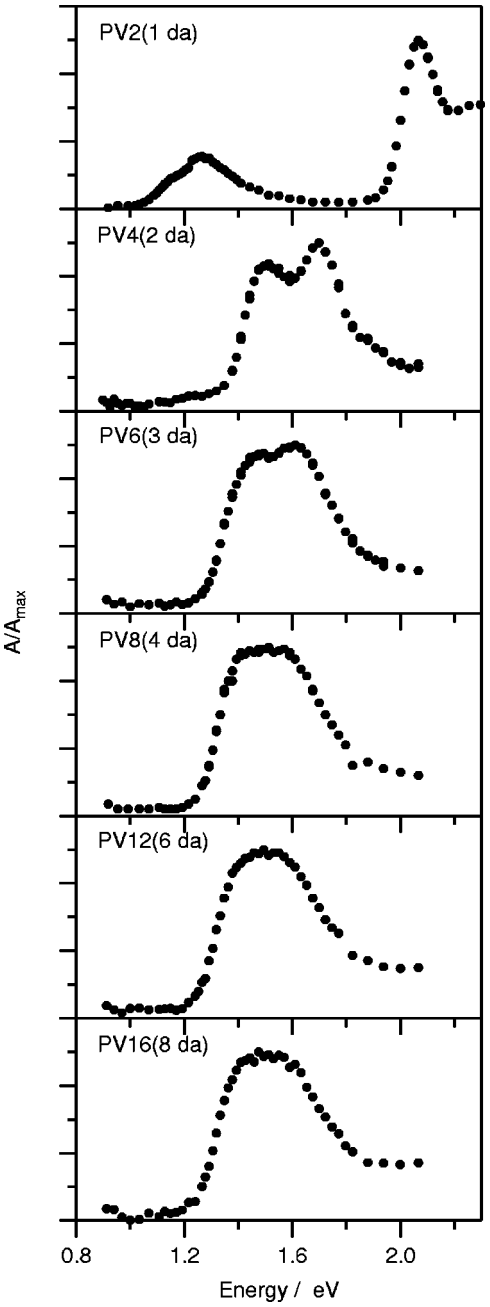

FIG. 3. Optical absorption spectra of the radical cations of the PVn($n/2\ da$) series.

very good, with most of the calculated energies differing by less than 0.15 eV from the experimental absorption maxima. In what follows we give a fuller discussion of the theoretical results and the comparison with experiment.

1. Unsubstituted oligomers, PVn

First, the unsubstituted PVn series is considered. The transition energies (ΔE_+), oscillator strengths and main CI expansion coefficients for this series are given in Table I. For the shorter oligomers up to PV3 two transitions with energies lower than the absorption onset of the neutral molecule are found. This is in agreement with the general appearance of spectra of singly oxidized PV's.[13,14] The agreement with the experimental ΔE_+ data improves in going from PV1 through

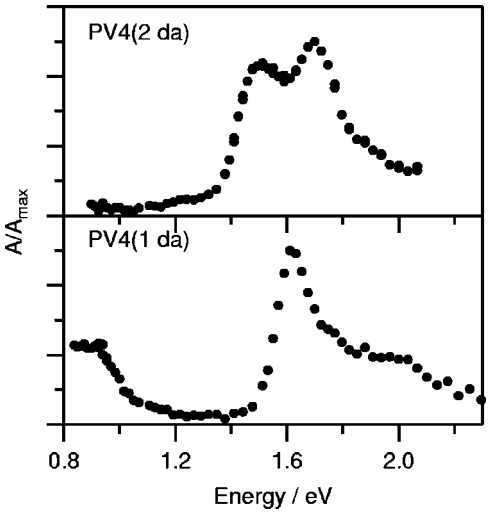

FIG. 4. A comparison of the optical absorption spectra of radical cations of PV4($2\ da$) and PV4($1\ da$).

PV3 which can be attributed to the use of a larger effective basis set upon increasing the size of the system studied.

For unsubstituted oligomers longer than PV3 there is no experimental data. The calculations show, however, that the radical cations of oligomers PV4 through PV12 should exhibit a third allowed transition in the spectrum, denoted RC3 in Table I.

As evident from Table I the RC1 transition is dominated in all cases by the configuration corresponding to an excitation from the doubly occupied HOMO (H) level to the singly occupied P1 level. In the following, such a configuration is denoted as (H→P1). The oscillator strength for RC1 increases markedly with the length of the oligomer, as observed also in earlier theoretical studies.[13]

For all PVn, the RC2 transition contains a large contribution from a configuration that corresponds to a singly excited determinant resulting from a transition from the singly occupied P1 orbital to the lowest unoccupied P2 orbital. This configuration is indicated as P1→P2. For longer oligomers the contribution from this transition to RC2 becomes somewhat less and configurations involving lower lying orbitals (such as H-2→P1 and H-4→P1) start mixing in more. These contributions due to lower lying orbitals is caused by a decrease of the energy difference between the orbital energy of P1 and the energies of the lower lying orbitals (H-2, H-4) as the chain length increases. This also leads to the formation of the third allowed transition which contains a considerable amount of P1→P2 character but also contributions such as H-2→P1 and H-4→P1.

Note that for the PVn series there are no contributions such as H-1→P1 and H-3→P1 to the allowed electronic transitions; see Table I. This can be understood by symmetry arguments. It was found that for PVn the frontier orbitals alternately have a_u and b_g symmetry, as illustrated in Fig. 1(b). Therefore the H-1→P1 configuration is due to a transition between orbitals that are both of b_g symmetry and therefore the transition dipole moment between these configurations is zero by symmetry. Thus these configurations do not contribute to the allowed electronic transitions. For

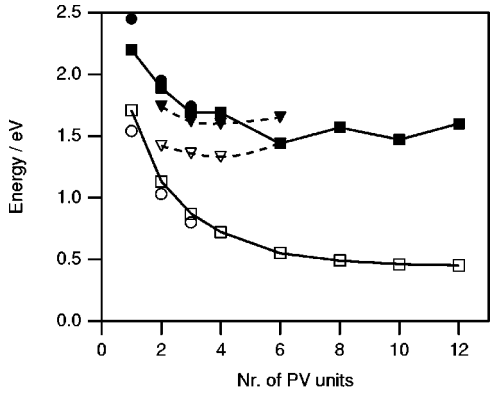

FIG. 5. The chain length dependence of the radical cation absorption energies RC1 (open symbols) and RC2 (closed symbols) determined experimentally (circles) or calculated (squares). The results of previous calculations by Cornil *et al.* (Ref. 13) are also shown (triangles).

RC2 the oscillator strength increases initially with chain length. However, when the third sub-gap absorption appears this trend is lost. In general, if the energies of the transitions RC1, RC2 and RC3 are compared it can be seen that RC1 is more sensitive to changes in the length of the chain than RC2 or RC3. RC1 decreases from 1.71 eV for PV1 to 0.49 for PV8, a decrease by a factor of 3.5 while RC2 decreases by less than 20%.

In Fig. 5 the transition energies for RC1 and RC2 are compared to experimental data from the work of Furukawa[14] (see also Table I) and to previous theoretical work by Cornil *et al.*[13] The correspondence between the present calculations and experimental data is very good for PV1 to PV3 and is considerably better than in the work of Cornil *et al.* The present method used to calculate the spectra is basically the same as that used by Cornil *et al.* The only difference is in the geometry used in the INDO/s-CIS calculation of the spectrum. Cornil *et al.* used geometries optimized using the semiempirical AM1 Hamiltonian, whereas in the present work the geometry optimizations were performed using density functional theory; see Sec. III. As will be shown below there are considerable differences between the geometries obtained with the AM1 and DFT methods.

The INDO/s-CIS method used here to calculate the excitation energies is especially parametrized for the calculation of absorption spectra of neutral molecules. The results obtained are usually very good if accurate molecular geometries are used in the calculations. The good correspondence between the excitation energies calculated in the present work and the experimental data therefore suggests that the geometries obtained from DFT calculations are more accurate than those obtained using the AM1 method, at least up to PV3. Due to the lack of experimental data for longer unsubstituted PV's it is not possible to draw definite conclusions about the quality of the geometry for these longer oligomers.

2. Fully dialkoxy substituted oligomers, PVn(n+1 da)

The cation absorption energies in the series of PV's containing two alkoxy substituents on all phenylene rings (PVn($n+1$ *da*)) are all lower than those in the corresponding unsubstituted PV's; see Tables I and II. The calculated results are in reasonable agreement with the experimental data obtained by Van Hal *et al.*[30] for these compounds; see Table II. Interestingly, the calculations show that there is a third sub-gap absorption band, even for the shortest oligomer of this series, PV2(3 *da*). A third absorption band is clearly present in the experimental spectra of Van Hal *et al.* However, this additional band is not assigned to a separate electronic transition by the authors. The calculated energy of RC3 agrees well with that obtained from the experimental spectra, see Table II. Also for the longer PV's studied by Van Hal *et al.* a second high energy band, or at least a shoulder towards the higher energy side of RC2, can be distinguished in the spectrum, in agreement with the calculated spectra.

In Table II the oscillator strengths and main CI-coefficients for the PVn($n+1$ *da*) oligomers are also given. The lowest energy transition is dominated by the H→P1 contribution in all cases, as was observed for the PVn series. For PV2(3 *da*) the second band, RC2, is mainly due to the P1→P2 configuration, while RC3 has predominantly H-2 →P1 character. For the longer oligomers the RC2 and RC3 bands cannot clearly be attributed to a single CI configuration. Both excited states are mixtures that consist mainly of P1→P2 and of configurations such as H-2→P2 and H-4 →P2. The introduction of the alkoxy side-chains effectively lowers the energy difference between these lower lying orbitals and P1. This causes the third absorption feature to appear already in PV2(3 *da*), while for the unsubstituted PV's the first appearance of RC3 was in PV4.

3. Partially dialkoxy substituted oligomers, PVn(n/2 da)

The PVn(n/2 *da*) oligomers are dialkoxy substituted on every second phenylene unit. The experimental radical cation spectra are shown in Fig. 3. The allowed transitions that were calculated for this series of oligomers are compared to the experimental data in Table III. The agreement is seen to be excellent. For PV2(1 *da*) both the calculated RC1 (1.26 eV) and RC2 (2.02) band are very close to the experimental values of 1.27 and 2.07 eV, respectively. For PV4(2 *da*) the low energy band RC1 is predicted to shift to a considerably lower energy (0.51 eV) which is lower than the experimental limit of *ca.* 0.9 eV. Accordingly it could not be experimentally observed. The energies of RC2 and RC3 are calculated to be 1.49 and 1.74 eV, respectively. This is in excellent agreement with the experimental spectrum in Fig. 3 which displays two maxima at 1.51 and 1.70 eV. The similar magnitude of the two bands is in agreement with the calculated oscillator strengths for RC2 and RC3 of 0.56 and 0.53, respectively. When the chain length is increased to PV6(3 *da*) the energy difference between the RC2 and RC3 bands becomes smaller; 0.25 eV for PV4(2 *da*) versus 0.09 eV for PV6(3 *da*), in agreement with the experimental spectra in Fig. 3. The calculated spectra for the longer oligomers show that increasing the chain length beyond PV6 has little further effect on RC2 and RC3 with both bands appearing close to 1.5 eV. Note that the calculated RC2 and RC3 energies actually increase slightly after $n=8$, see Table III. This is probably due to the fact that the largest CI expansions used

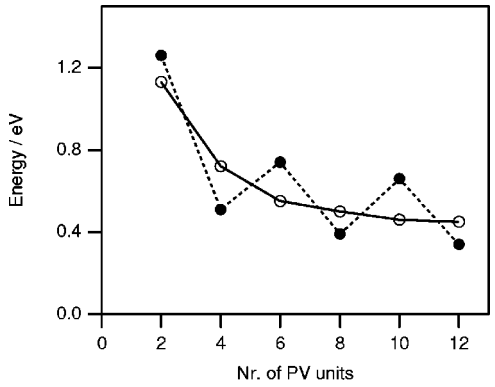

FIG. 6. A comparison of the calculated transition energy corresponding to the lowest energy absorption band, RC1, of the unsubstituted PV series, PVn (open circles, solid line) and the partially dialkoxy substituted series, PVn($n/2\,da$) (filled circles, dashed line) as a function of chain length.

here are still not sufficient. As mentioned in Sec. III the RC2 and RC3 energies are more sensitive to the size of the CI expansion than RC1.

When the calculated RC1 energies are considered, an intriguing odd/even trend emerges. Figure 6 shows a comparison of the chain length dependence of the RC1 energy for the PVn($n/2\,da$) series and the unsubstituted PVn series. The PVn($n/2\,da$) oligomers with an even number of dialkoxy substituted phenylene rings all have an RC1 energy lower than that obtained for the corresponding PVn derivative, whereas for those PVn($n/2\,da$) oligomers with an odd number of dialkoxy substituted phenylene rings the energy is always higher than that of the unsubstituted analoge. It is worth noting that for the ''odd'' compounds the central phenylene ring is dialkoxy substituted but unsubstituted for the ''even'' compounds. This odd–even effect is discussed in more details below when the effect of the substitution pattern on the charge distribution is considered.

4. Effect of the dialkoxy substitution pattern

In order to investigate the effect of the substitution pattern on the electronic properties of the PV cations in more detail the compound PV4($1\,da$) with dialkoxy substitution only at the central phenylene moiety was investigated. The low energy RC1 band of this compound is predicted to shift to considerably higher energy compared to the spectra of PV4 and PV4($2\,da$). This large blue shift of the RC1 band of PV4($1\,da$) is observed experimentally as shown in Fig. 4.

These results show that the precise position of an alkoxy group can have a considerable effect on the delocalization length of a charge on the phenylene vinylene chain. This means that there must be a significant mixing of the p-type orbitals on the oxygen atom of the alkoxy groups with the p-orbitals of the conjugated π-system. The highest occupied molecular orbital in PV4($1\,da$) obtained from INDO/s calculations was indeed found to have significant density on the oxygen atom in the side chain. Therefore the angle between the alkoxy group and the plane of the conjugated chain can be expected to have a pronounced influence on the energy of RC1. The calculated data given in Tables II and III for alkoxy substituted PV's refer to the geometry in which the dihedral angle between the side chain and the conjugated chain is zero; i.e., the carbon atoms of the methoxy groups are in the plane of the molecule. This planar configuration was found to be the minimum energy geometry. When the substituents are twisted to a dihedral angle of 90 degrees the energy of RC1 becomes 0.86 eV, which is 0.17 eV lower than found for the planar geometry. This shows that the orientation of the substituents indeed influences the degree of delocalization of the charge.

C. Effect of substituents on the charge distribution

More direct insight into the effect of the substituents on the delocalization of a charge carrier on a phenylene vinylene oligomer can be obtained by examining the actual charge distribution along the PV chain. In Fig. 7 the distributions of an excess positive charge on phenylene vinylene tetramers with different substitution patterns are shown. The charge distributions were obtained from a Mulliken population analysis performed on the same wave functions used to calculate the electronic absorption spectra; i.e., the INDO charge distribution. The figure shows the increase in positive charge, Δ_+, on the (dialkoxy-)phenylene and vinylene moieties in the chain when an electron is removed. This increase was calculated by adding the Mulliken charges on all atoms in a unit and subtracting the charge that was present on that unit in the neutral molecule.

For the unsubstituted oligomer a maximum in the charge distribution is found at the central phenylene unit of the chain. In general the vinylene units have a lower charge density than their neighboring phenylene units. The presence of more charge on the phenylene units is related to a considerably lower ionization potential of these units compared with the vinylene units. The introduction of methoxy substituents on the phenyl rings leads to a further lowering of their ionization potential which is accompanied by a further shift of charge from the vinylene groups to the phenyl rings as evident from Fig. 7. If only the central phenylene ring contains methoxy groups, as in PV4($1\,da$), almost 40% of the charge becomes localized there. If methoxy substituents are present on the second and fourth phenyl ring, PV4($2\,da$), the charge is more evenly distributed than in PV4. The lowering of the ionization potential of these two phenylene units leads to an increase of positive charge on these rings, accompanied by a decrease of charge on the middle phenylene ring and its neighboring vinylene units. Finally, if all phenylene rings are dialkoxy substituted, as in the PV4($5\,da$) oligomer, the charge distribution is almost the same as found for the unsubstituted PV4 oligomer.

In order to gain more insight into the relationship between the charge distribution and the radical cation optical absorption spectra presented above, it is useful to express the degree of delocalization of charge in terms of the so-called ''participation ratio,'' P, which is defined as

$$P=\left[\sum_{i=1}^{N} Q_i^2\right]^{-1}, \tag{5}$$

where Q_i is the amount of charge present on the ith unit and N is the number of monomer units. P is equal to 1 if the all

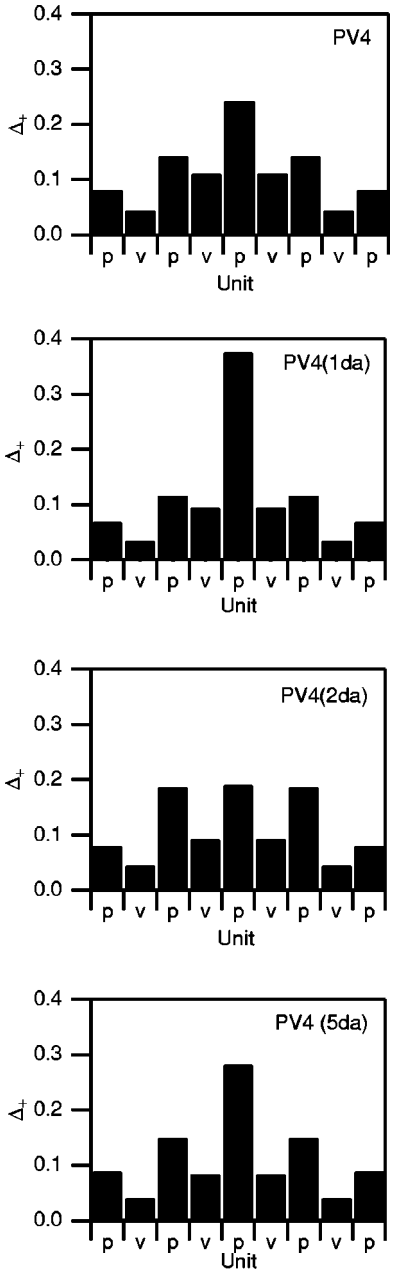

FIG. 7. Effect of dialkoxy substitution on the distribution of an excess positive charge, Δ_+, in PV tetramers with different dialkoxy substitution patterns obtained from Mulliken population analysis on wave functions obtained from an INDO/s calculation. Phenylene and vinylene moieties are indicated by p and v, respectively.

of the excess charge is localized on a single unit while $P=N$ if a charge is evenly spread over all N units of a chain. The participation ratio was calculated for PV oligomers with different substitution patterns by taking for Q_i the increase in charge on the phenylene and vinylene units upon the introduction of a charge. The calculated values of P for selected oligomers are listed in Table IV.

First consider the values for the unsubstituted PV oligomers. The value of P gradually increases with increasing chain length, indicating an increased degree of delocalization. This increase in the degree of delocalization is accompanied by a gradual decrease of the lowest cation absorption energy RC1 (See Table I).

TABLE IV. Participation ratio, P [see Eq. (5)] from INDO/s Mulliken population analysis. Values of P from the DFT charge distribution are given in parentheses.

Compound	P	Compound	P
PV2	4.6 *(4.6)*	PV2(1 *da*)	3.3 *(4.2)*
PV4	7.1 *(8.3)*	PV4(2 *da*)	7.2 *(7.5)*
PV6	8.2 *(12.0)*	PV6(3 *da*)	6.1 *(10.9)*
PV8	8.6 *(15.6)*	PV8(4 *da*)	8.8 *(14.1)*
PV4(1 *da*)	5.1 *(7.7)*		
PV4(5 *da*)	6.4 *(7.4)*		

If two methoxy groups are substituted at the central phenylene unit of PV4 to give PV4(1 *da*), P decreases to 5.1 which is significantly smaller that the value of 7.1 for PV4 but close to the value of 4.6 found for PV2. Therefore it is concluded that in PV4(1 *da*) the charge is delocalized over a distance similar to the degree of delocalization in PV2. This result directly explains the very similar RC1 absorption energies of these two molecules; i.e., 1.13 and 1.03 eV for PV2 and PV4(1 *da*), respectively.

At this point it is interesting to recall the odd–even trend in the RC1 energies for the PVn(n/2 *da*) oligomer series, shown in Fig. 6. For PV2(1 *da*) a higher RC1 energy is found than for PV2. This is consistent with the values for P which are 4.6 and 3.3 for PV2 and PV2(1 *da*), respectively. The presence of the methoxy substituents on the middle ring causes a more localized charge distribution and therefore a lower P. For PV4(2 *da*) the RC1 energy is lower than that for PV4 due to the more delocalized charge, the values of P for PV4(2 *da*) is slightly larger that for PV4. The presence of methoxy groups on the second and fourth phenylene units "draws" the charge away from the middle ring leading to a more evenly distributed charge as illustrated in Fig. 7. For PV6(3 *da*) the calculated RC1 energy is considerably higher than for both PV4(2 *da*) and PV6, which is consistent with the lower value of P for PV6(3 *da*). For PV8(4 *da*) the RC1 energy is lower than that for PV8 in agreement with the higher value of P. According to these INDO/s calculations, the presence of methoxy substituents on the central phenylene ring [in PV3(1 *da*), PV6(3 *da*) and PV10(5 *da*)] leads to a more localized charge distribution. If methoxy substituents are not present on the central ring but only on phenylene rings closer to the chain ends, the charge is drawn away from the middle, which gives a more delocalized charge distribution leading to lower RC1 energies.

It should be noted that the calculation of the participation ratio using the Mulliken charges obtained from the DFT calculation yields a different result. The differences between the INDO and DFT charge distribution are discussed in more detail below.

D. Geometry changes upon introduction of a charge

The removal of an electron from a phenylene vinylene chain is known to result in deformations of the geometry, most prominently seen as changes of the C–C bond lengths. Previously Cornil *et al.*[13] have shown, using semi-empirical AM1 calculations, that these geometry deformations are not

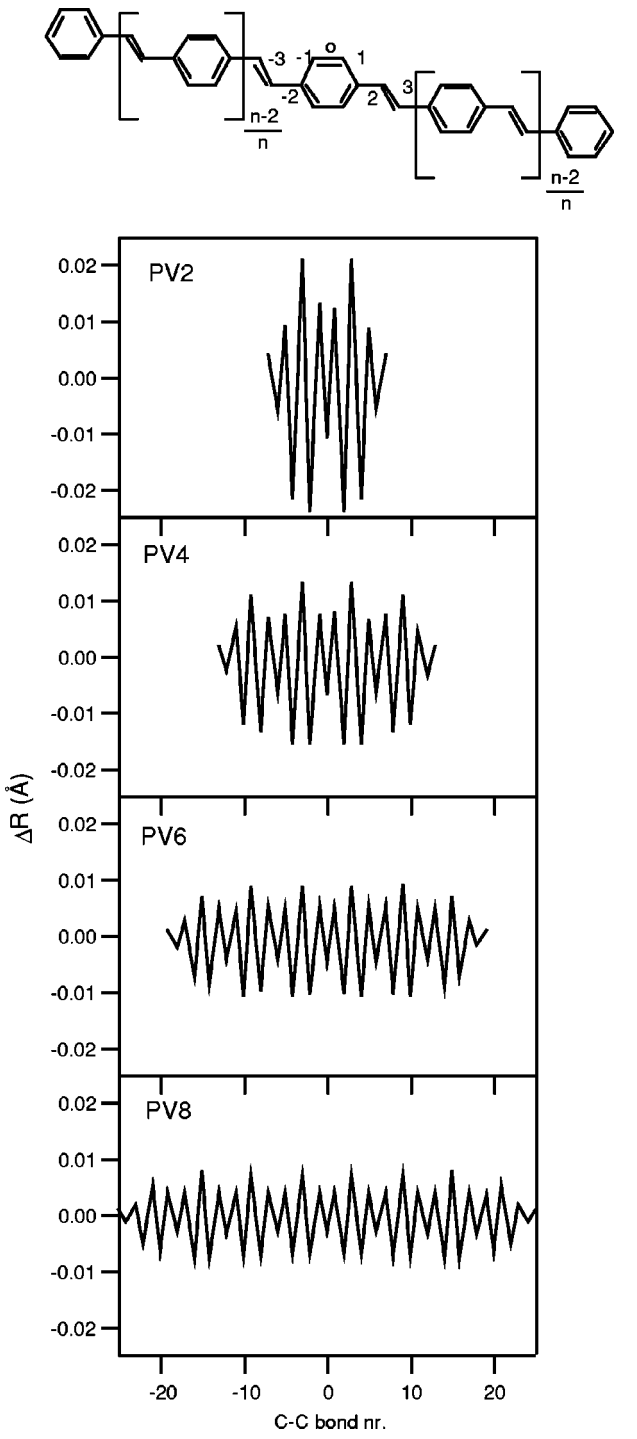

FIG. 8. Changes in C–C bond length upon removal of an electron for the unsubstituted PVn series from DFT calculations. The numbering of the bonds is indicated in the scheme.

uniformly distributed over the whole phenylene vinylene chain. The geometry deformations were calculated to extend over a chain length encompassing approximately only three phenylene vinylene units. The changes in the C–C bond lengths outside this three-unit central region were found to be negligible.

When the geometry deformations that are obtained from the present DFT calculations are considered, a different picture emerges. Figure 8 shows the changes in C–C bond lengths in PV2, PV4, PV6 and PV8. The numbering of the C–C bonds is indicated in Fig. 8. As evident from this figure, the maximum change in C–C bond length is ~ 0.02 Å for PV2. The largest changes are found in the vinylene units and the bonds between the vinylene units and the phenyl rings, the bond length changes in the phenylene units are considerably smaller. Upon increasing the length of the PV oligomers the C–C bond changes become smaller, for PV8 the maximum change is less than 0.01 Å. The introduction of alkoxy substituents has no significant effect on the geometry deformations.

TABLE V. Ionization energies and relaxation energies calculated using DFT for selected PV's.

Compound	E_{ion} in eV	E_{relax} in eV
PV1	7.882	0.105
PV2	7.131	0.081
PV3	6.723	0.066
PV4	6.462	0.056
PV6	6.146	0.040
PV8	5.956	0.033
PV10	5.824	0.025
PV12	5.724	0.022

The results described here are very different from the earlier work by Cornil *et al.*[13] who found C–C bond length changes up to ~ 0.04 Å in the central part of the molecule. Furthermore, the geometry deformations in the DFT calculations are evenly spread over the whole PV chain and exhibit no features characteristic of the formation of a self-localized polaron, in contrast to the earlier AM1 results. Similar differences between DFT and Hartree–Fock calculations have been found for thiophene oligomers. Moro *et al.*[34] have performed DFT geometry optimizations for thiophenes and also found that the geometry deformation was evenly spread over the entire oligomer while earlier AM1 calculations[35] yielded a polaron localized on five thiophene rings.

The smaller geometry changes in longer PV's are consistent with the smaller relaxation energies, see Table V. The relaxation energies were obtained from the DFT calculations as the difference between the vertical ionization energy, also given in Table V, and the adiabatic ionization energy. As expected, the ionization energy was found to decrease gradually with increasing chain length. The relaxation energy is 0.08 eV for PV3 and decreases to close to 0.02 eV for PV12 which is comparable to the thermal energy at room temperature ($k_B T \approx 0.025$ eV at 293 K). This means that, according to the present DFT calculations, the formation of a self-trapped polaron, as predicted by AM1 calculations, is unlikely. The DFT results therefore suggest that the existence of localized charges in solids should be attributed to impurities or defects in the films or crystals.[36] These defects can be of a chemical nature, such as polymerization mistakes causing cross-links or broken conjugation.[37] Moreover, the localization of charges can be induced by conformational defects caused by inter-chain interactions.

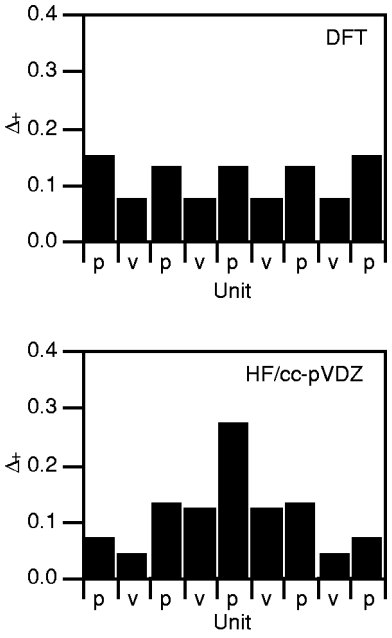

FIG. 9. Distribution of excess positive charge, Δ_+, in PV4 from DFT and HF/cc-pVDZ calculations. Phenylene and vinylene moieties are indicated by p and v, respectively.

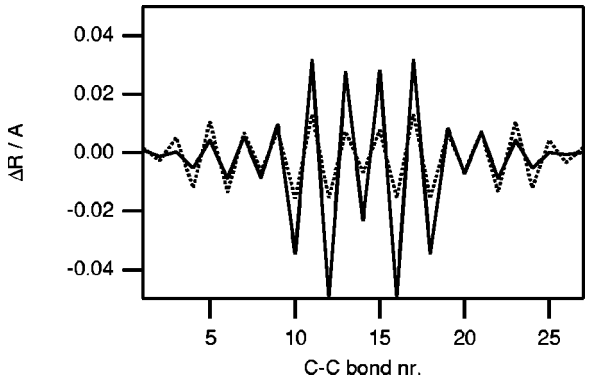

FIG. 10. Changes in C–C bond length on abstraction of an electron from PV4. A comparison of DFT/DZP (dotted line) and HF/cc-pVDZ (solid line) results.

E. Comparison of DFT results with Hartree–Fock calculations

As mentioned in the previous sections, there are considerable differences between results obtained using DFT and those using HF methods. DFT calculations are known to give a more delocalized charge distribution for charged conjugated oligomers.[34,38,39] In Fig. 9 the charge distribution for PV4 obtained from a Mulliken population analysis of the charge density obtained from the DFT calculations is shown. The charge distribution is evenly spread over the entire PV chain, with more charge on the phenylene rings than on the vinylene moieties. This result is in agreement with the delocalized geometry deformations obtained from DFT calculations as shown above. *Ab initio* Hartree–Fock (HF) calculations performed on PV4 using Dunning's cc-pVDZ basis set[40] (which is of similar quality as the DZP-type basis set consisting of Slater functions used in ADF) give results very similar to the charge distribution from the INDO/s Hartree–Fock calculations as evident from a comparison of Figs. 7 and 9(b). The same difference between DFT and HF calculations is observed in the geometry deformations shown in Fig. 10. The deformations obtained from the HF/cc-pVDZ calculations occur mostly in the vinylene units in the middle of the chain, and are very small in the outermost units. Note that the C–C bond length change is about 0.04 Å in the *ab initio* HF calculations, similar to the earlier semi-empirical AM1 calculations.[13]

There can be several explanations for these large differences between Hartree–Fock and DFT. In the DFT calculations electron correlation is included, which can lead to a more evenly spread charge distribution. However, there are also indications that in DFT the delocalization of a charge on a conjugated chain is overestimated.[41] The good agreement between the spectra calculated using INDO/s-CIS with DFT geometries and experimental spectra suggests that the geometry deformations in PV cations are evenly distributed over the whole chain. However, it should be realized that the good agreement may be fortuitous since a combination of a uniform geometrical deformation (DFT) and a more localized charge distribution (INDO/s) is used. The INDO/s calculation is a Hartree–Fock type calculation and does not contain a (dynamic) correlation. The charge distribution that is obtained from the INDO/s calculation has a rather localized character, even if no substituents are present (see PV4 in Fig. 7). The use of a delocalized geometry deformation opposes this tendency to localize leading to a sort of half-way charge distribution.

These differences between DFT and HF are also reflected in the odd–even effect for the PVn($n/2\,da$) series. The oscillating behavior of the RC1 energy is consistent with the degree of delocalization (e.g., reflected in the participation ratio; Table IV) calculated from the INDO/s charge distribution. However, if the values of P obtained from the DFT charge distributions are considered (see Table IV in parentheses) a gradually decreasing trend is observed.

It seems clear that the delocalization length of a polaron on a conjugated chain obtained from Hartree–Fock calculations is too small. The polaron ''size'' of 3 or 4 PV units obtained from AM1 calculations implies that no changes in the optical absorption spectra should be observed for oligomers longer than this. In the experimental results by Van Hal *et al.*[30] the energy of RC1 decreases gradually up to the longest PV studied in that work, which contains seven phenylene units. Moreover, for thiophene oligomers, AM1[35] calculations have predicted a polaron confined to approximately five thiophene rings, while changes in the radical cation spectra up to a thiophene oligomer containing twelve rings have been observed experimentally.[42] This indicates that HF calculations underestimate the spatial extent of charge carriers on conjugated chains considerably, probably due to the absence of (dynamic) electron correlation. DFT calculations have been performed for singly charged thiophene oligomers by Moro *et al.*[34] and by Brocks[38] and both found results similar to those obtained here for phenylene vinylenes; i.e., the charge distribution and geometry deformations are fully delocalized over the entire chain.

It would be of interest to establish whether the larger delocalization of the charge in DFT calculations is caused by the inclusion of electron correlation or is an artifact in the DFT calculations. This issue could be resolved by comparison with correlated calculations at the MP2 level of theory. This requires the use of large basis sets suitable for calculations including electron correlation such as, for example, the correlation-consistent series of basis sets constructed by Dunning.[40] Such calculations should be performed on PV oligomers of at least *circa* 8 repeat units and would require large computational power. Therefore these calculations are beyond the scope of the present work.

It is of particular importance to extend the experimental data on cations of PV's. Cation spectra for PVn($n/2\,da$) should be extended to lower photon energies in order to establish whether there is actually an odd/even effect in the RC1 energies. This would make it possible to decide which charge distribution is more reliable, that of the INDO/s wavefunction that predicts an odd–even trend or that from the DFT charge distribution where the degree of delocalization increases gradually with the chain length.

V. SUMMARY AND CONCLUSIONS

In this paper we describe a combined experimental and theoretical study of electronic and structural properties of radical cations of phenylene vinylene (PV) oligomers. PV cations in solution were produced using pulse radiolysis. The cation optical absorption spectra were measured for a variety of PV's differing in chain length and substitution pattern. The introduction of alkoxy substituents was found to have a large effect on the optical absorption spectra of the cations. The cation optical absorption spectrum was found to depend strongly on the pattern of substitution. This indicates that substituents influence the degree of delocalization considerably.

INDO/s-CIS calculations of the cation optical absorption spectra have been performed using geometries optimized by density functional theory (DFT) calculations. The resulting absorption energies for the cations were found to be in excellent agreement with experiments. This shows that the combination of DFT geometries with an INDO/s-CIS calculation of the electronic spectra gives a reliable way of predicting cation spectra of conjugated oligomers. It was found that for several oligomers a third and sometimes a fourth sub-gap absorption feature can arise especially for longer oligomers. These findings are in full agreement with experimental results.

An analysis of the charge distribution along the PV chains shows that the presence of alkoxy substituents can lead to a more localized charge if the substituents are not present on all phenylene rings. The degree of delocalization correlates with the radical cation absorption spectrum. The lowest energy absorption band, RC1, was shown to be most sensitive to charge delocalization. For a series of PV oligomers containing alkoxy substituents on every second phenylene ring an interesting odd/even effect in the energy of the low energy absorption band, RC1, is predicted. This odd/even effect correlates with the degree of delocalization of the charge obtained from the INDO/s wavefunction. The RC1 energy is higher if substituents are present on the middle phenylene ring and lower if no substituents are present there. These predictions could not be verified experimentally since the optical absorption occurs at energies outside the range accessible in the experimental setup used in this work. Different results for the degree of delocalization were obtained from the DFT charge distribution. It is therefore of considerable interest to extend the experimental spectra to lower energies.

Large differences were observed between the charge distributions obtained from DFT calculation and those obtained using Hartree–Fock theory. Hartree–Fock calculations show the formation of a stable self-trapped polaron, in agreement with earlier HF calculations. In contrast, according to the DFT results a positive charge is almost evenly distributed over the entire PV chain up to an oligomer containing twelve repeat units which argues against the formation of a self-trapped polaron. Therefore, on basis of the DFT results it should be concluded that the presence of localized charges in bulk solids or in solution should be attributed to defects, such as polymerization mistakes or disordered chain conformations. Additional quantum chemical calculations (such as the MP2 calculation) are called for in order to establish whether the DFT method gives a correct description of charges on conjugated chains.

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